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The Measurement of the Conductivity of Electrolytes in very Dilute Solutions

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THE MEASUREMENT OF THE CONDUCTIVITY OF ELECTROLYTES IN VERY DILUTE SOLUTIONS

BY

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1912

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

MASTER OF ARTS

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1914

1914
B17

UNIVERSITY OF ILLINOIS

THE GRADUATE SCHOOL

June 1, 1914

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

ROBERT EARL BAKER

ENTITLED THE MEASUREMENT OF THE CONDUCTIVITY OF ELECTROLYTES IN VERY DILUTE SOLUTIONS

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF ARTS

E. W. Washburn
In Charge of Major Work

W. A. Noyes
Head of Department

Recommendation concurred in:

Committee on Final Examination

284532

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I. INTRODUCTION.

At the basis of the complete and correct interpretation of the results of any investigation into the properties of electrolytes, is the accurate determination of the equivalent conductance at infinite dilution. This value enters into all investigations in which the concentrations of the ions and of the unionized molecules are desired. The accepted way of expressing the degree of ionization γ is given by the equation:

$$\gamma = \frac{\Lambda}{\Lambda_0} f\left(\frac{\eta}{\eta_0}\right),$$

in which Λ is the equivalent conductance at the concentration used, Λ_0 the equivalent conductance at infinite dilution, and $f\left(\frac{\eta}{\eta_0}\right)$ some function of the viscosity of the solution.

Various methods have been employed for the determination of Λ_0. The most important of these are the method of Kohlrausch, in which he makes use of algebraic equations, and the graphic method of Noyes. Both of these men employ special cases of the general equation,

$$\Lambda_0 = \Lambda + K C^k \Lambda^h$$

in which k is a constant the value of which lies between 1 and 0, and h is a constant greater than, or equal to 0.

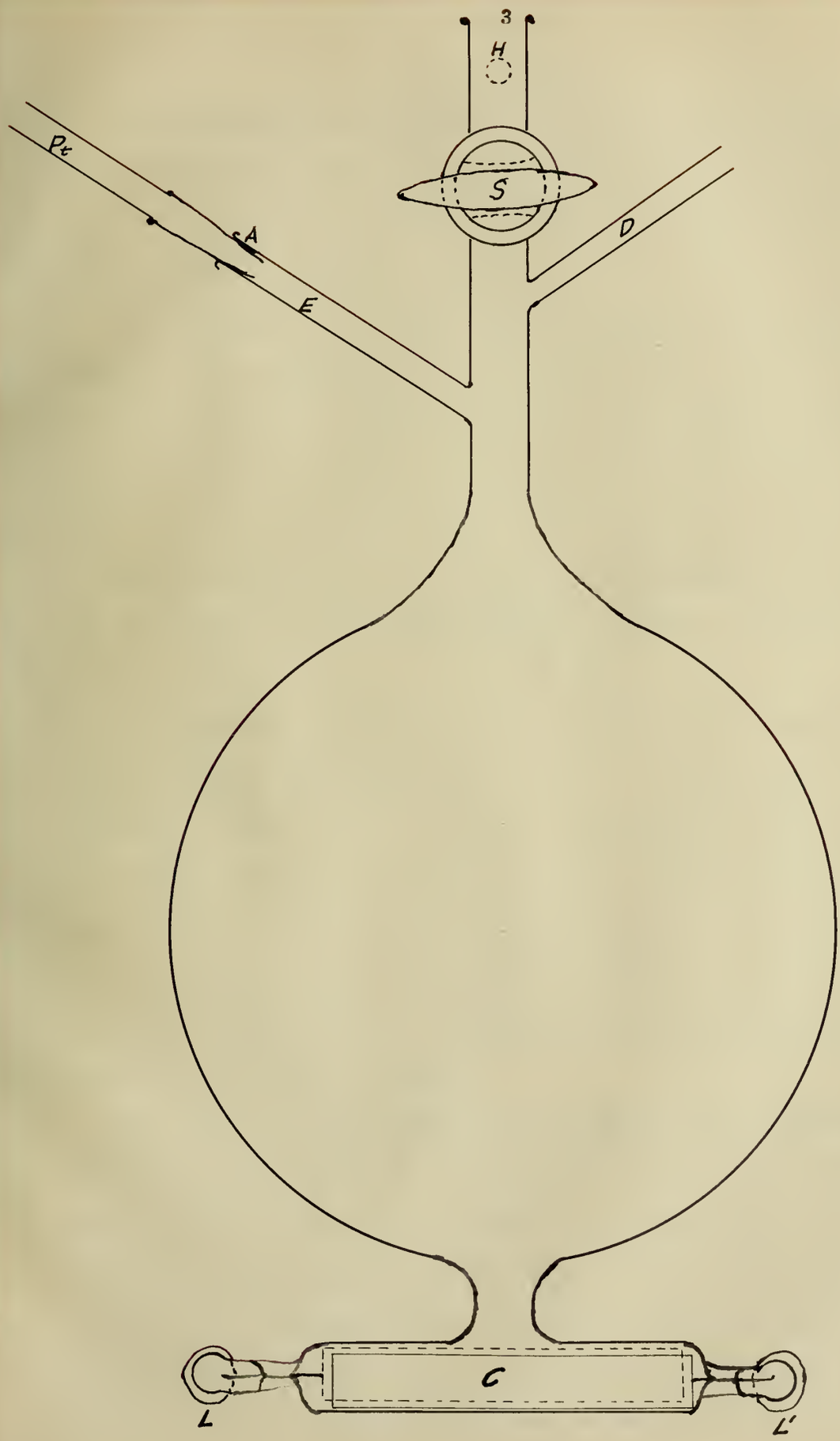
Bates has shown (J.A.C.S., 35, May, 1913) that, altho Λ_0 cannot be determined exactly theoretically, never-the-less it can be determined between an upper and a lower limit. He shows that the more dilute solution for which the conductivity data is accurately known, the smaller the difference between these limits. For example, data for .0001 N KCl solution gives differences between the limits and the mean value of 0.1%, while that of .001 N gives a difference of 0.7%. However, the accuracy of these theoretical limits depends on the accuracy of the conductivity data used. Thus we cannot put too much confidence in the theoretical results calculated from the data of Kohlrausch, for in many of his determinations for solutions

of .0001 N, the arbitrary water correction amounted to as much as 10% of the conductivity of the electrolyte. Also, in the theoretical calculation, it is assumed that Oswald's Dilution Law holds for solutions from the lowest concentration used down to infinitely dilute solutions. It is important therefore, to devise some method for the accurate determination of the conductivity of solutions below .0001 N. It is my purpose to describe a method by which it is hoped that these results may be obtained.

II. APPARATUS.

In making investigations into solutions of electrolytes in these low concentration ranges, it is necessary to make measurements with a very high degree of precision. The electrical apparatus used is the same as that described by Washburn and Bell (J.A.C.S., 35, Feb., 1913.). However, it is found that, by cutting out all the resistance in the starting box, the motor can be driven at its normal frequency from a fifty-five volt storage battery supply which insures a steady speed.

The cell that is employed is shown in the diagram on page 3. The large platinum electrodes are sealed into the compartment marked C. This electrode compartment is sealed into the bottom of a 1500 cc. round bottom jena flask B. At the top of the flask is a large jena tube with a stop cock S, two side tubes, E and D, and a back tube H. Pt is a platinum tube sealed into jena glass and connected to E by means of the ground glass joint A. The platinum tube is used for the purpose of making connections with the tin delivery tube from the still by means of soldering. Tube E serves as an entrance tube for the vapor from the still. Tube B serves both as an exhaust and as a drain tube. L and L' are terminals for the electrodes. The leads from L and L' are protected by thick walled rubber tubing.


3
H
Pt
S
A
D
E
C
L
L'

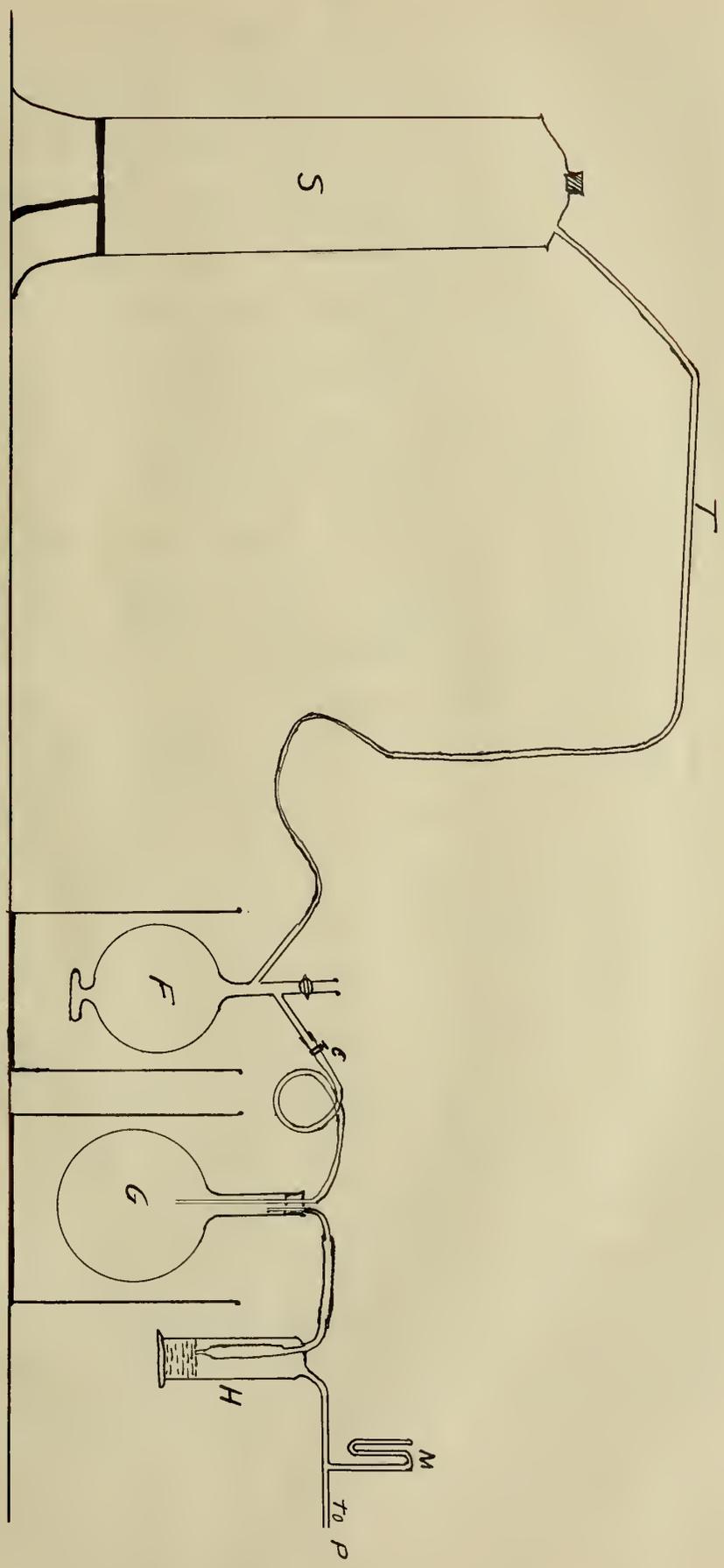
III. METHOD.

With the electrical apparatus referred to above, the measurement of the conductivity of very dilute solutions and even of water itself can be made with a precision of .01% with ordinary care, and with special care a precision of .001% may be obtained.

The attainment of an equal degree of accuracy in the conductance depends on the elimination of the constant sources of error, the chief of which is due to the impurities found in the conductivity water when it is allowed to come in contact with the atmosphere. The purest water that Kohlrausch was able to obtain under such conditions was $.58 \times 10^{-6}$; but by repeated distillationsin a vacuum and pouring the distillate back into the supply water, he was able to obtain water with a conductivity as low as $.404 \times 10^{-7}$.

The impurities in the water are got rid of in my work by the following process. Ordinary distilled water is run into a special still where it is treated with about 150 cc. of alkaline permanganate solution which breaks up the organic substances that may be present forming ammonia. The ammonia passes off in the first 1/3 of the distillate. Then the steam from this still is condensed into a third still of 25 liters capacity, where it is treated with from 3 to 5 cc. of phosphoric acid which neutralizes any organic bases that may be present.

The diagram on page 5 shows the arrangement of the apparatus. The still S is connected thru the tin condensing tube T to flask F which contains the electrodes. F is connected thru a large flask G, a sulfuric acid flask H, and a manometer M to a pump P. F and G are surrounded by ice baths. T is surrounded by a water jacket. The whole system is exhausted by means of the pump. The stop cock C between F and G is closed, the temperature of S is raised slightly and the water distills from S and


S
T
F
E
G
H
M
To P

collects in F, where its conductivity is measured. If the conductivity is found to be too great, F is inverted, the stop cock C opened and the contents of F drained into G. The stop cock is again closed, F returned to its original position, and the distillation begins again. While the distillation is taking place, G is removed and emptied, then replaced and evacuated and is ready to receive the next drainage from F. This process is repeated until pure water is obtained.

When pure water is once obtained, the arms E and D are sealed. A 10cc. portion of a .0001 N solution is placed in a capsule in the tube above the stop cock S, Fig.1., a stopper is inserted above the capsule and the space exhausted thru the small back tube H. Then the stop cock is turned and the capsule dropped into the main body of the cell. This gives a solution of about.000001 N. The cell is then placed in a thermostat and allowed to come to constant temperature of 25° and its conductivity measured. A second portion of the solution is added in the same way as the first and its conductivity measured. This process is repeated until the solution reaches a concentration of .001 N. The cell is then weighed, emptied of its contents, thoroly cleaned and dried and weighed again. The difference between the two weighings gives the weight of the original water plus the weights of the portions of solution added. Each separate portion of the solution added is carefully weighed, and since its concentration is accurately known, the concentration of the resulting solutions can be easily calculated.

So far, the results obtained have been unsatisfactory. This may be due to impurities from the soldered joint in the delivery tube which have not had sufficient rinsing to become thoroly clean, or to impurities in the stop cock grease used.

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